



Short communication

Methacrylate based gel polymer electrolyte for lithium-ion batteries

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HIGHLIGHTS

- Methacrylate based gel polymer electrolytes as promising electrolyte for lithium-ion batteries.
- Methacrylate based gel polymer electrolytes display high conductivity and good mechanical stability.
- Methacrylate based gel polymer electrolytes allow performance comparable to that obtained using conventional electrolytes.

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ABSTRACT

A methacrylate based gel polymer electrolyte (GPE) was prepared and electrochemically investigated. The polymer was synthesized as a statistical co-polymer of oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and benzyl methacrylate (BnMA) by free radical polymerization. The ethylene glycol side chain of OEGMA should be able to interact with the liquid electrolyte, thus keeping it inside the GPE, whereas BnMA was used to enhance the mechanical stability of the GPE. Such a polymer was able to retain liquid electrolyte up to 400% of its own weight, while the mechanical stability of the GPE was still high enough to be used as separator in lithium-ion batteries. The GPE displayed a conductivity of 1.8 mS cm^{-1} at 25°C and an electrochemical stability window comparable to that of a standard liquid electrolyte. When used in lithium-ion batteries, such a GPE allowed a performance comparable to that obtained using conventional liquid electrolytes. Therefore the reported electrolyte was identified as a promising candidate as electrolyte for lithium-ion batteries.

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1. Introduction

Today's main applications of lithium-ion batteries are in portable electronic devices. Recently, they have been also considered for application in transportation [1], such as electric vehicles (EVs) or hybrid electric vehicles (HEVs), and for stationary energy storage systems [2,3].

In state of the art lithium-ion batteries usually liquid electrolytes consisting of a lithium salt (e.g. LiPF_6) dissolved in a mixture of organic carbonates are used [4,5], which display a low boiling point and flash point and are prone to leakage. Moreover, this hazardous potential increases with increasing battery size. To avoid the risk of electrolyte leakage solid polymer electrolytes (SPEs), which consist of a lithium salt dissolved in a polymer matrix, have been developed. Among these electrolytes, the ones based on poly(ethylene oxide) (PEO) have been widely investigated and showed the best properties. [6] These electrolyte systems enable the construction of

light-weighted and flexible all-solid-state batteries in various forms and shapes [7]. Additionally, the costs for the separator can be saved, as the mechanical stability of SPEs is high enough to avoid electronic contact between the anode and cathode. Unfortunately, SPEs suffer from low conductivity at ambient temperatures (in the range of 10^{-6} to $10^{-4} \text{ S cm}^{-1}$) which limits their application to higher temperatures [8,9]. Beside their low conductivity, also the oxidative stability of PEO has been reported to be only 3.8 V vs. Li/Li^+ which limits the cathodes that can be used with these electrolytes to those operating at 3 V [10].

To combine the advantage of liquid electrolytes (high ionic conductivity) with those of SPEs (no separator needed, avoiding cell leakage) GPEs have been introduced [11]. In these systems a liquid electrolyte is immobilized into a polymer matrix. Therefore, high conductivities can be achieved, while the mechanical stability of the system remains high enough to be used as separator in lithium-ion batteries. Different polymers have been investigated as host systems, e.g. poly(methyl methacrylate), poly(acrylonitrile), poly(-vinylidene fluoride) or co-polymers of these systems [12–17].

Among the many polymers investigated in this context methacrylate based systems have the advantage of wide availability, low

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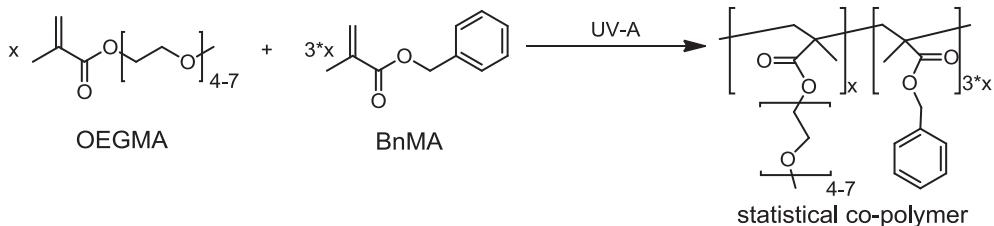


Fig. 1. Polymerization of oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and benzyl methacrylate (BnMA) by UV light.

toxicity and good electrochemical stability [18,19]. Additionally, polymethacrylates can be synthesized by irradiation with UV-light, which is a fast and cheap synthesis method. Recently, methacrylate based polymer membranes containing ethylene oxide side chains have attracted some attention [20–22]. These systems display high conductivities and good electrochemical stabilities. However, the applicability of these polymer membranes has just been shown in lithium metal systems in combination with lithium iron phosphate (LFP) as cathode material up to a potential of 4.0 V.

In this paper we report on the preparation, electrochemical characterization and application of GPEs with high ionic conductivity and good mechanical stability. The polymer matrix of this GPE was synthesized by UV-induced photopolymerization of two different methacrylate monomers, oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and benzyl methacrylate (BnMA) (Fig. 1). OEGMA was chosen because the ethylene glycol side chains should be able to interact with the liquid electrolyte, thus keeping it inside the polymer avoiding cell leakage. On the other hand, BnMA was used to enhance the mechanical stability of the GPE. The polymer membranes obtained by this method are able to retain liquid electrolyte up to 400% of its own weight, while the mechanical stability of the obtained GPE is still high enough to be used as separator in lithium-ion batteries. The applicability of this electrolyte was proven in LFP/graphite and $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (NCM)/graphite full cells.

2. Experimental

2.1. Polymer synthesis

In Fig. 1 the reaction equation of the considered synthesis is shown.

The monomers OEGMA (Sigma–Aldrich, average Mn = 300) and BnMA (Sigma–Aldrich, 96%) were mixed in a molar ratio of 1:3. 0.2 wt% of the radical starter benzophenone (Acros Organics, 99%) were dissolved in the solution and the reaction mixture was polymerized by irradiation with UV light (UVACUBE 100, Hoenle AG) for 1 h. During irradiation, the mixture was placed between two Mylar foils and a constant film thickness of 300 or 600 μm was adjusted. After polymerization the membranes were dried over night in a glass oven (Büchi Labortechnik AG) at 120 °C under vacuum.

After punching out polymer discs with a diameter of 7–10 mm the polymer membranes were gelled with 1 M LiPF_6 in EC:DMC 1:1 (LP30 Merck, battery grade) by adding an appropriate amount of electrolyte to the polymer. The electrolyte was soaked into the polymer over night in sealed glass vessels. Polymer:liquid electrolyte ratios ranging from 60 wt% polymer content and 40 wt% liquid electrolyte up to 20 wt% polymer content and 80 wt% liquid electrolyte have been investigated.

2.2. Electrochemical characterization

The conductivity of the GPEs was investigated in a sealed cell between two stainless steel electrodes with a distance of 300 μm .

Electrode preparation and assembling of the cell was carried out in an argon filled glove box (MBraun, O_2 and H_2O content lower than 1 ppm). The influence of the polymer:liquid electrolyte ratio was determined at 25 °C. The temperature dependant conductivity between 5 °C and 55 °C was investigated for a composition of 20 wt % polymer:80 wt% liquid electrolyte in an environmental simulation chamber (MK 53, Binder GmbH). All conductivity measurements have been performed using a Solartron 1260 impedance analyzer, connected to a Solartron 1287A potentiostat/galvanostat, in a frequency range from 1 MHz to 10 Hz.

All tests with active materials were performed in three-electrode cells (Swagelok) with lithium as reference electrode to monitor the electrode potentials. For electrochemical stability measurements a GPE consisting of 20 wt% polymer and 80 wt% liquid electrolyte was placed between a lithium counter (12 mm diameter) and a Pt working electrode (1 mm diameter) inside a Swagelok cell with lithium as reference electrode. The stability was determined by cyclic voltammetry using a Solartron 1287 potentiostat with a scan rate of 1 mV s^{-1} in a potential range from open circuit potential (OCP) to 6.5 V vs. Li/Li^+ for the anodic sweep (=oxidation) and from OCP to 0.1 V vs. Li/Li^+ for the cathodic sweep (=reduction).

For constant current charge/discharge cycling, anodes and cathodes of the same capacity have been chosen, whereas for cyclic voltammetry experiments the capacity of the working electrode was only 70% of the counter electrode capacity to ensure that the current is not limited by the counter electrode. In order to ensure an optimal contact between the particles of the electrode and the GPE, the electrodes were pre-wetted with liquid electrolyte. After the cells were connected to a battery tester Series 4000 from MACCOP, Inc. they were allowed to rest for 6 h before the constant current cycling started. LFP/graphite cells were cycled in a voltage range between 2.8 and 4.1 V. Herein 1C corresponded to current density of 0.4–0.6 mA cm^{-2} . For NCM/graphite full cells the voltage range was between 2.8 and 4.2 V and 1C corresponded to a current density of 1.75 mA cm^{-2} . Cyclic voltammetry measurements on LFP and graphite working electrodes were performed using a scan rate of 50 and 30 mV s^{-1} , respectively.

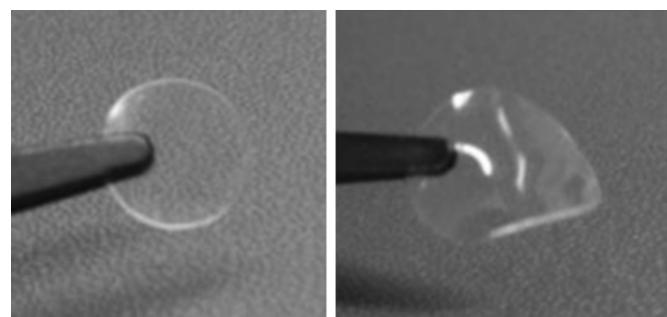


Fig. 2. Photographs of the polymer membranes before and after gelling.

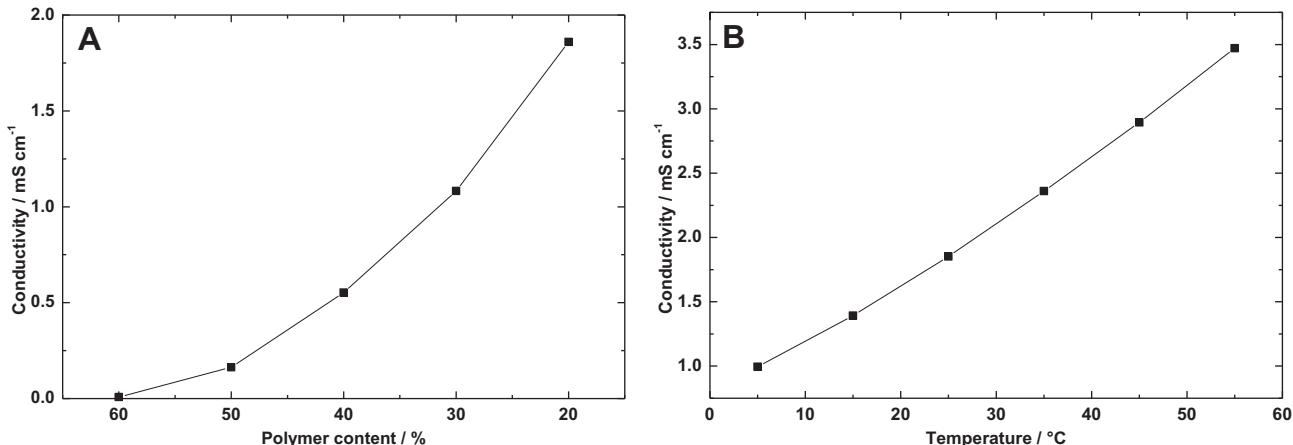


Fig. 3. A) Dependence of the ionic conductivity on the polymer:liquid electrolyte ratio. B) Temperature dependence of the conductivity of a GPE consisting of 20% polymer and 80% 1 M LiPF₆ in EC:DMC 1:1.

2.3. Electrode preparation

Graphite electrodes were prepared in a composition of 90 wt% TIMREX T44 graphite (TIMCAL Graphite & Carbon), 5 wt% conducting agent (SuperC65, TIMCAL Graphite & Carbon) and 5 wt% PVdF binder (Kynar 761, Arkema). After dissolving the binder in *N,N*-dimethylformamide (DMF, Sigma–Aldrich) the graphite and the conducting agent were added. The resulting slurry was cast on a copper foil using a doctor blade. After drying, electrodes with a diameter of 12 mm were punched out and dried over night in a glass oven (Büchi Labortechnik AG) at 120 °C under vacuum.

LFP electrodes were prepared by the same method by mixing 84 wt% LFP (SüdChemie), 4 wt% SFG 6L (TIMCAL Graphite & Carbon), 4 wt% SuperC65 (TIMCAL Graphite & Carbon) and 8 wt% PVdF binder (Solef 1013/1001, Degussa) in *N*-methylpyrrolidone (NMP, Sigma–Aldrich).

For NCM/graphite full cells electrodes provided by Evonik Industries were used.

All cell tests were performed in full cell arrangement and the capacities are calculated based on the cathode mass.

3. Results and discussion

Mixtures of OEGMA, BnMA and benzophenone were polymerized by irradiation with UV light. The goal was the preparation of films with the highest possible content of OEGMA while maintaining the mechanical properties of the films in order to be able to use them both as electrolyte and separator. A high amount of OEGMA was desirable as this component should be able to interact with the liquid electrolyte thus, retaining it inside the polymer. Additionally, it is expected that the conductivity increases with the content of OEGMA as more electrolyte can be immobilized into the polymer. A molar ratio of 1:3 (OEGMA:BnMA) was found to be the best compromise between interaction with liquid electrolyte and mechanical stability. These systems contained a high amount of OEGMA while displaying a mechanical stability allowing the preparation of self-standing films. Therefore, all further experiments were carried out with these polymers. The obtained films were subsequently swollen with liquid electrolyte (1 M LiPF₆ in EC:DMC 1:1) to give GPEs.

In Fig. 2 photographs of the polymer membranes before and after gelling with liquid electrolyte are shown. It can be seen, that by our synthesis method transparent, self-standing polymer membranes are obtained. These membranes are highly flexible and

nonbrittle, which is an important requirement for their application as GPEs for lithium-ion batteries. The membranes were able to retain liquid electrolyte up to a composition of 20% polymer and 80% liquid electrolyte. After gelling, the membranes are still self-standing and their mechanical stability remains high enough to be used as separator.

3.1. Electrochemical characterization

To realize high performance lithium-ion batteries, electrolytes with high ionic conductivity are required. As in GPEs the lithium ions can be either complexed by the liquid solvent molecules (EC and DMC) or by the oxygen atoms in the polymer (oligo ethylene glycol side chain or ester groups), the conductivity strongly depends on the polymer to liquid electrolyte ratio. Therefore, the conductivity of the GPE was determined as a function of the polymer and liquid electrolyte fraction. It can be seen from Fig. 3A that the conductivity increases with increasing liquid electrolyte content and conductivities above 1.8 mS cm⁻¹ can be achieved for a GPE consisting of 20 wt% polymer and 80 wt% liquid electrolyte. The increase of conductivity with increasing liquid electrolyte content can be explained on the one hand by a higher salt concentration in the gel and on the other hand by a higher amount

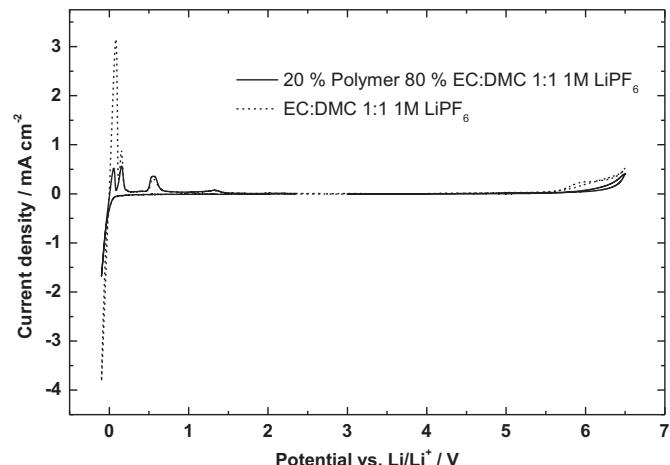


Fig. 4. Electrochemical stability window of the GPE and liquid electrolyte. Working electrode: Pt. Reference and counter electrode: Li. Scan rate: 1 mV s⁻¹.

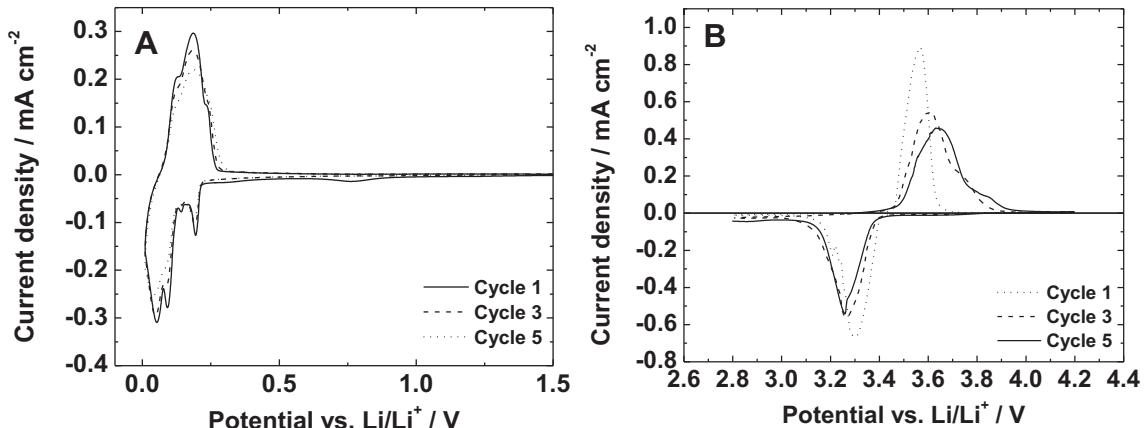


Fig. 5. A) CV of a graphite electrode. Counter electrode: LFP. Reference electrode: Li. Electrolyte: 20% polymer, 80% 1 M LiPF₆ in EC:DMC 1:1. Scan rate: 30 μ V s⁻¹. B) CV of a LFP electrode. Counter electrode: graphite. Reference electrode: Li. Electrolyte: 20% polymer, 80% 1 M LiPF₆ in EC:DMC 1:1. Scan rate: 50 μ V s⁻¹.

of solvent molecules (EC and DMC) which allow a higher mobility of the ions. As in lithium-ion batteries a high conductivity of the electrolyte is desired, the composition with the highest conductivity (20 wt% polymer, 80 wt% liquid electrolyte) was chosen for all further characterizations. For this GPE the temperature dependency of the conductivity was determined as shown in Fig. 3B. At 25 °C the conductivity of this GPE is above 1.8 mS cm⁻¹ and increases with temperature up to 3.5 mS cm⁻¹ at 55 °C. Even at 5 °C still a conductivity of 1 mS cm⁻¹ can be achieved. For comparison, the conductivity of SPEs at room temperature is often several orders of magnitude lower than the values obtained with our GPE [14,23]. On the other hand, conductivities of liquid electrolytes widely used in lithium-ion batteries are in the mS cm⁻¹ range [24]. Considering that, the conductivity of the GPE appears high enough for use in lithium-ion batteries.

As the operation potential of the electrodes has to be within the electrochemical stability window (ESW) of the electrolyte, a wide ESW is desired. To determine the ESW of the GPE cyclic voltammetry on Pt electrodes was performed. The potential of the working electrode was scanned with 1 mV s⁻¹ from the open circuit potential (OCP) of the cell to 6.5 V vs. Li/Li⁺ for oxidative sweep and to -0.1 V vs. Li/Li⁺ for reductive sweep. Afterwards, it was scanned back to the OCP of the cell. For comparison also the ESW of the pure liquid electrolyte (1 M LiPF₆ in EC:DMC 1:1) was determined under identical conditions. The results of these experiments are shown in Fig. 4. During the reductive sweep, a similar behaviour of the two electrolytes is observed. Lithium plating starts at the same potential

for both electrolytes. When the current is reversed (at -0.1 V vs. Li/Li⁺) both electrolytes show the same signals. Only the observed current density is lower for the GPE which can be explained by the lower conductivity of this electrolyte compared to the liquid electrolyte. A similar behaviour is also occurring during anodic sweep. Again, an increase in current density is observed for both electrolytes in the same potential region. As already mentioned for the reductive sweep, the current density of the GPE is lower than the one of the liquid electrolyte. As the oxidative reactions are irreversible, no reduction peaks are observed when scanning the potential back from 6.5 V to OCP.

The results of this experiment indicate that the investigated GPE displays an ESW comparable to that of the liquid electrolyte immobilized into the gel. Especially, the high oxidative stability of the GPE was unexpected, because of the oligo ethylene glycole side chains in the polymer matrix, which are known to decompose at higher potentials [10]. As the ESW of our GPE is as wide as the one of the standard electrolyte its application in combination with active materials for lithium-ion batteries was investigated.

3.2. Cell tests

As the electrochemical characterization of the reported GPE identified this system as a promising candidate for use in lithium-ion batteries, its applicability was investigated in combination with common electrode materials. To prove that no irreversible reactions of the GPE are occurring at the electrodes CVs on graphite

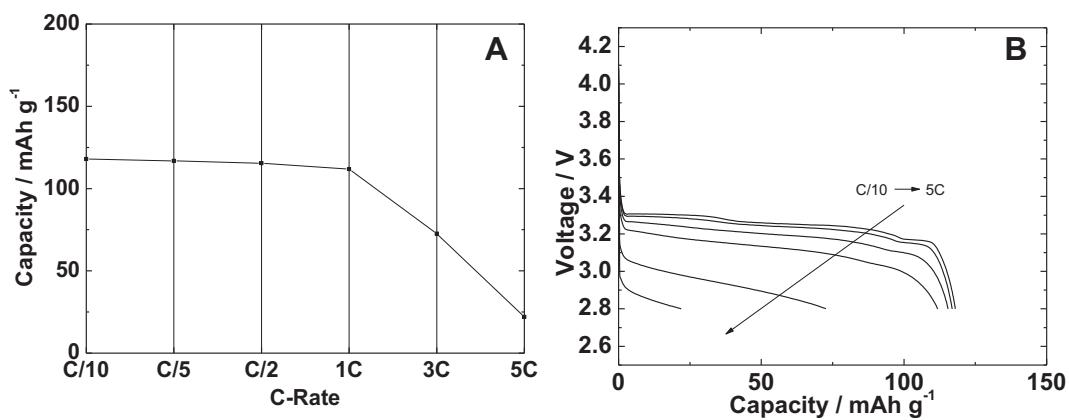


Fig. 6. C-rate test of an LFP/graphite full cell. Charge at C/10, discharge at different C-rates from C/10 up to 5C. Potential range: 2.8–4.1 V vs. Li/Li⁺. A) Capacity as a function of discharge rate. B) Voltage profiles of the cell at different discharge rates.

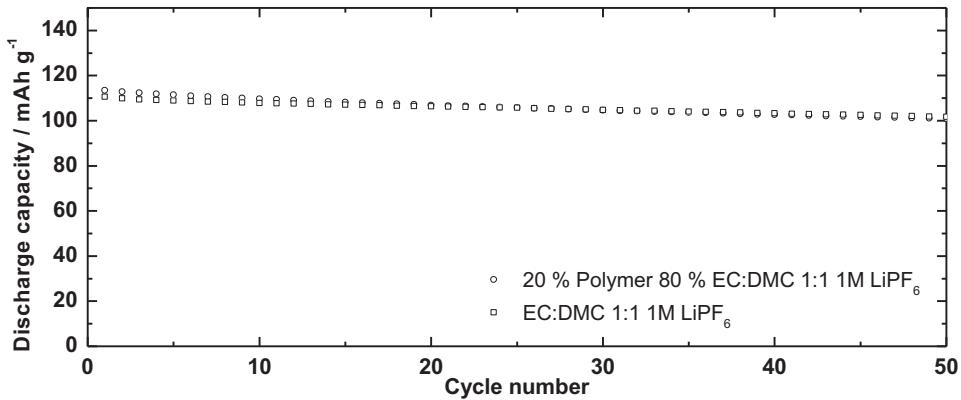


Fig. 7. Constant current cycling of a LFP/graphite full cell. Charge and discharge was performed at C/2. Potential range: 2.8–4.1 V vs. Li/Li⁺.

anodes and LFP cathodes have been performed. In Fig. 5A the voltammogram of the anode is shown. In the first cycle an irreversible reaction is observed at 0.75 V vs. Li/Li⁺ which is due to SEI [25] formation on graphite. In all following cycles only the lithium intercalation and deintercalation signals into graphite are observed. This experiment shows that the investigated GPE is electrochemically stable on graphite electrodes. The GPE can not only be used in lithium metal batteries, but also in lithium-ion batteries.

Beside the stability of the electrolyte in combination with graphite electrodes, also the stability on LFP cathodes has been investigated (Fig. 5B). The CVs of the LFP electrodes display the typical shape and peaks around 3.5 V vs. Li/Li⁺. However, the intensity of the oxidation signal decreases during the following cycles. This is most likely due to the loss of lithium caused by the SEI formation on graphite, which was used as counter electrode. Additionally, we expected to observe an increase in current density above 4 V vs. Li/Li⁺ as ethylene oxide containing electrolytes are known to decompose at higher potentials [10]. However, only the oxidation and reduction signals of the active material are observed in Fig. 5B, indicating that the GPE is stable in the potential range of commonly used cathode materials.

To investigate the applicability of the electrolyte in lithium-ion batteries LFP/graphite full cells have been tested. First three formation cycles were performed at C/10, with efficiencies of 79%, 97% and 98%, respectively. After the formation of the cell a C-rate test was performed. Herein the cell was charged at C/10 and discharged at different C-rates ranging from C/10 to 5C. As shown in Fig. 6 the achieved capacity decreases only slightly up to a C-rate of 1C. Only at higher C-rates a significant capacity decrease was observed.

After the C-rate test the cell was cycled at C/2 for 50 cycles. For comparison, also a cell with liquid electrolyte was cycled under the same conditions. As shown in Fig. 7, both cells display a very similar behaviour. Initially they achieve a capacity of about 110 mAh g⁻¹. After 50 cycles the capacity of the cells is still as high as 100 mAh g⁻¹. As both cells show a similar capacity decrease it can be concluded that this is not caused by the GPE, but most likely by a degradation of the electrodes.

Due to the good electrochemical stability and cycling behaviour of the electrolyte in combination with lab scale LFP and graphite electrodes, also full cells with NCM and graphite electrodes, provided by an industry partner, were investigated. Also in this case three formation cycles at C/10 were initially performed, followed by a C-rate test. In the first cycle already an efficiency of 87% was achieved. In all following cycles the efficiencies were between 99% and 100%. The results of the C-rate test (Fig. 8) are similar to those observed in LFP/graphite full cells. Up to 1C the capacity decreases only slightly: At C/10 a capacity of 148 mAh g⁻¹ was achieved, while at 1C the capacity was still as high as 119 mAh g⁻¹, which is 80% of the capacity obtained at C/10. Only at higher C-rates the capacity decreases significantly.

Also the long term cycling stability of a NCM/graphite full cell containing the GPE was investigated (Fig. 9). After three formation cycles at C/5 the cell was cycled at C/2. After an initial decrease of capacity, caused by the C-rate increase from C/5 to C/2, the cell shows a very stable cycling behaviour and a capacity of 118 Ah g⁻¹. After 200 cycles the cell still reaches a capacity of 110 mAh g⁻¹ which corresponds to a capacity retention of 93%. For comparison also a cell with liquid electrolyte was tested under the same

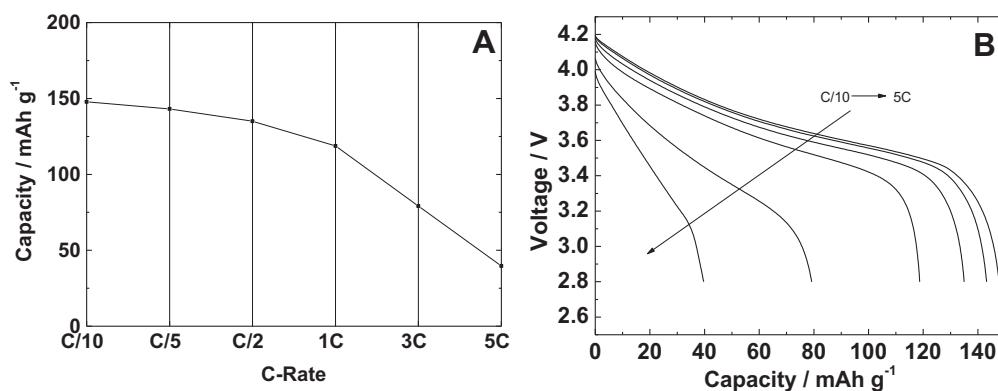


Fig. 8. Rate test of a NCM/graphite full cell. Charge at C/10 + constant voltage (4.2 V), discharge at different C-rates from C/10 up to 5C. Potential range: 2.8–4.2 V vs. Li/Li⁺. A) Capacity as a function of discharge rate. B) Voltage profiles of the cell at different discharge rates.

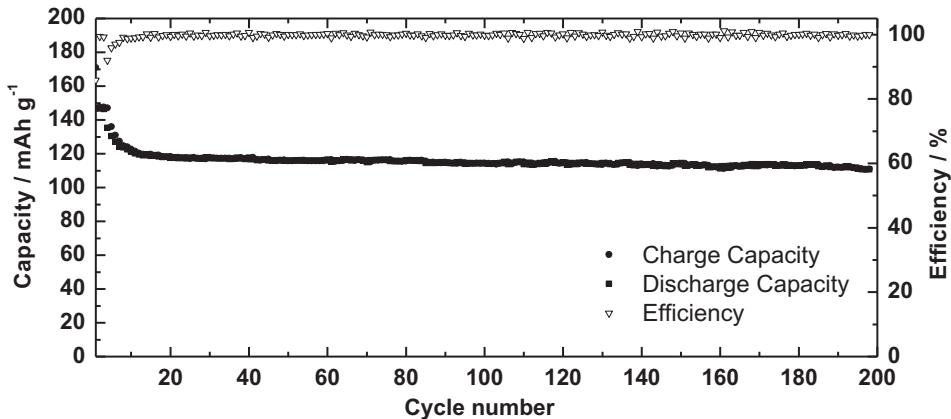


Fig. 9. Constant current cycling of a NCM/graphite full cell. Charge at C/2 + constant voltage (4.2 V), discharge at C/2. Potential range: 2.8–4.2 V vs. Li/Li⁺.

conditions (data not shown). This cell achieved a similar capacity retention. The results of these tests clearly show that the investigated electrolyte can be used with standard materials for lithium-ion batteries.

4. Conclusion

In this study we reported on the preparation, electrochemical characterization and application of a methacrylate based GPE for lithium-ion batteries. OEGMA and BnMA were polymerized by irradiation with UV light and the received polymer was able to retain 400% of its own weight of liquid electrolyte. The mechanical stability of such GPE was high enough to be used as separator in lithium-ion batteries. A conductivity of 1.8 mS cm⁻¹ was achieved at 25 °C and the electrochemical stability window on Pt was as wide as the one of the liquid electrolyte immobilized into the gel. The applicability of the electrolyte was proven in LFP/graphite as well as NCM/graphite full cells. During the C-rate test only a slight decrease in capacity was observed for both systems up to a C-rate of 1C. Moreover, the cells comprising the GPE showed a cycling stability comparable to that of cells based on conventional liquid electrolytes.

Considering these results, the investigated GPE appears as a promising candidate for lithium-ion batteries.

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